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## INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

(Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference P60188PCT	<b>FOR FURTHER ACTION</b> See Form PCT/IPEA/416	
International application No. PCT/EP2004/012851	International filing date (day/month/year) 09.11.2004	Priority date (day/month/year) 19.11.2003
International Patent Classification (IPC) or national classification and IPC C07D241/46, C25D3/38		
Applicant ATOTECH DEUTSCHLAND GMBH et al		
<p>1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 5 sheets, including this cover sheet.</p> <p>3. This report is also accompanied by ANNEXES, comprising:</p> <p>a. <input checked="" type="checkbox"/> sent to the applicant and to the International Bureau a total of 12 sheets, as follows:</p> <p><input checked="" type="checkbox"/> sheets of the description, claims and/or drawings which have been amended and are the basis of this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions).</p> <p><input type="checkbox"/> sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. I and the Supplemental Box.</p> <p>b. <input type="checkbox"/> (sent to the International Bureau only) a total of (indicate type and number of electronic carrier(s)) , containing a sequence listing and/or tables related thereto, in computer readable form only, as indicated in the Supplemental Box Relating to Sequence Listing (see Section 802 of the Administrative Instructions).</p>		
<p>4. This report contains indications relating to the following items:</p> <p><input checked="" type="checkbox"/> Box No. I Basis of the opinion</p> <p><input type="checkbox"/> Box No. II Priority</p> <p><input type="checkbox"/> Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability</p> <p><input type="checkbox"/> Box No. IV Lack of unity of invention</p> <p><input checked="" type="checkbox"/> Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement</p> <p><input type="checkbox"/> Box No. VI Certain documents cited</p> <p><input type="checkbox"/> Box No. VII Certain defects in the international application</p> <p><input type="checkbox"/> Box No. VIII Certain observations on the international application</p>		
Date of submission of the demand  28.04.2005	Date of completion of this report  08.12.2005	
Name and mailing address of the international preliminary examining authority:   European Patent Office - P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Pays Bas Tel. +31 70 340 - 2040 Tx: 31 651 epo nl Fax: +31 70 340 - 3016	Authorized Officer  Allard, M  Telephone No. +31 70 340-2002 	

**INTERNATIONAL PRELIMINARY REPORT  
ON PATENTABILITY**

International application No.  
PCT/EP2004/012851

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**Box No. I Basis of the report**

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1. With regard to the **language**, this report is based on the international application in the language in which it was filed, unless otherwise indicated under this item.
- ☐ This report is based on translations from the original language into the following language, which is the language of a translation furnished for the purposes of:
- ☐ international search (under Rules 12.3 and 23.1(b))
  - ☐ publication of the international application (under Rule 12.4)
  - ☐ international preliminary examination (under Rules 55.2 and/or 55.3)
2. With regard to the **elements\*** of the international application, this report is based on *(replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report)*:

**Description, Pages**

1-4, 6-27	as originally filed
5, 5a	received on 28.04.2005 with letter of 22.04.2005

**Claims, Numbers**

1-29	received on 28.04.2005 with letter of 22.04.2005
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- ☐ a sequence listing and/or any related table(s) - see Supplemental Box Relating to Sequence Listing
3. ☐ The amendments have resulted in the cancellation of:
- ☐ the description, pages
  - ☐ the claims, Nos.
  - ☐ the drawings, sheets/figs
  - ☐ the sequence listing (*specify*):
  - ☐ any table(s) related to sequence listing (*specify*):
4. ☐ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).
- ☐ the description, pages
  - ☐ the claims, Nos.
  - ☐ the drawings, sheets/figs
  - ☐ the sequence listing (*specify*):
  - ☐ any table(s) related to sequence listing (*specify*):

\*. If item 4 applies, some or all of these sheets may be marked "superseded."

**INTERNATIONAL PRELIMINARY REPORT  
ON PATENTABILITY**

International application No.  
PCT/EP2004/012851

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**Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

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1. Statement

Novelty (N)	Yes: Claims	1-29
	No: Claims	-
Inventive step (IS)	Yes: Claims	1-29
	No: Claims	-
Industrial applicability (IA)	Yes: Claims	1-29
	No: Claims	-

2. Citations and explanations (Rule 70.7):

**see separate sheet**

**Re Item V**

**Reasoned statement with regard to novelty, inventive step or industrial applicability;  
citations and explanations supporting such statement**

Reference is made to the following documents:

D4: PATENT ABSTRACTS OF JAPAN vol. 009, no. 188 (C-295), 3 August 1985 (1985-08-03) & JP 60 056086 A (HODOGAYA KAGAKU KOGYO KK), 1 April 1985 (1985-04-01)

**Novelty (Article 33(2) PCT)**

The compounds of claims 1-9 are not disclosed in the available prior art: the subject-matter of claims 1-9, 22-26 and 29 is therefore novel.

The single vessel method of claims 10-21 is not disclosed in the available prior art, whereby the subject-matter of these claims is novel.

The available prior art does not disclose electrodeposition of copper on printed circuit boards or on semiconductor substrates according to claims 27 and 28, whose subject-matter is therefore also novel.

**Inventive step (Article 33(3) PCT)**

D4, which is considered to represent the closest prior art, describes phenazinium derivatives useful as additives to improve copper-electrodeposition from plating baths.

In the light of the teachings of D4 the problem underlying and solved (see comparative examples of the description) by the present application can be seen in the provision of an improved process for copper-electrodeposition.

The use of the novel compounds, or of the purified compounds (not as mixtures), according to the present application to solve this problem is not suggested by the

**INTERNATIONAL PRELIMINARY  
REPORT ON PATENTABILITY  
(SEPARATE SHEET)**

International application No.

**PCT/EP2004/012851**

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teachings of the available prior art, and involves therefore an inventive step.

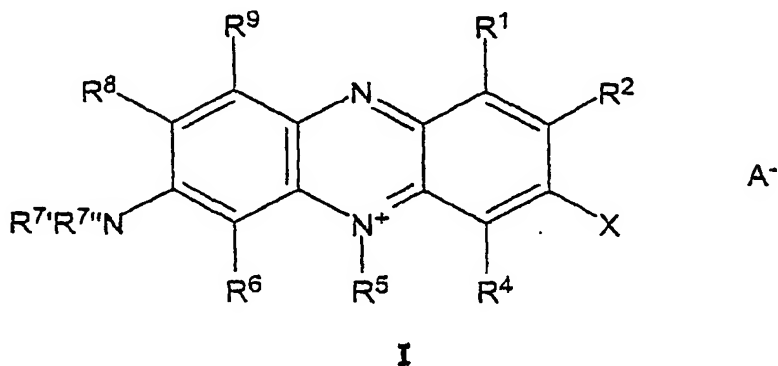
Industrial applicability (Article 33(4) PCT)

The compounds, processes and compositions of claims 1-29 can be used in the electrochemical industry.

Claims:

(91)

- 5 1. Halogenated or pseudohalogenated monomeric phenazinium compounds of a purity of at least 85 mole-% having the following general chemical formula:



10

wherein

15

$R^1, R^2, R^4, R^6, R^7, R^7'', R^8$  and  $R^9$  are selected independently of each other from a group comprising hydrogen, halogen, amino, aminoalkyl, hydroxy, cyano, thiocyanate, isothiocyanate, cyanate, isocyanate, mercapto, carboxy, the salt thereof, carbonic acid ester, sulfo, the salt thereof, sulfoester, lower alkyl, unsubstituted aryl, substituted aryl, heteroaryl and alicyclic heteroradicals,

20

$R^5$  is selected from a group comprising lower alkyl, unsubstituted aryl, substituted aryl and heteroaryl,

X is a halogen or a pseudohalogen and

$A^-$  is an acid anion.

\* < insert text of page 28a >

25

2. The phenazinium compounds according to claim 1, characterized in that  $R^1, R^2, R^4, R^6, R^7, R^7'', R^8$  and  $R^9$  are selected independently of each other from a group comprising hydrogen and lower alkyl.

with the requirement that, if X is halogen, the phenazinium compounds are selected from the group, comprising

- 5      i) 3-chloro-7-N,N-dimethylamino-2-methyl-5-phenyl-phenazinium salt,  
      ii) 3-bromo-7-N,N-dimethylamino-2-methyl-5-phenyl-phenazinium salt, and  
      iii) 3-bromo-7-N,N-diethylamino-5-phenyl-phenazinium salt.

3. The phenazinium compounds according to claim 2, characterized in that lower alkyl is methyl or ethyl.

4. The phenazinium compounds according to any one of the preceding claims, characterized in that  $R^5$  is aryl.

5. The phenazinium compounds according to claim 4, characterized in that aryl is phenyl.

~~16. The phenazinium compounds according to any one of the preceding claims, characterized in that X is chlorine, bromine or thiocyanate.~~

~~7.~~ The phenazinium compounds according to any one of the preceding claims, characterized in that they are selected from a group comprising

- i) ~~3-chloro-7-N,N-dimethylamino-2-methyl-5-phenyl-phenazinium salt,~~  
ii) ~~3-bromo-7-N,N-dimethylamino-2-methyl-5-phenyl-phenazinium salt,~~  
iii) ~~3-bromo-7-N,N-diethylamino-5-phenyl-phenazinium salt and~~  
iv) ~~7-amino-2,8-dimethyl-3-thiocyanato-5-phenyl-phenazinium salt.~~

~~8.~~ The phenazinium compounds according to <sup>any one of the preceding claims</sup> ~~claim 7~~, characterized in that the salt is selected from a group comprising chloride, bromide, hydrogen sulfate and tetrafluoroborate.

~~9.~~ The phenazinium compounds according to <sup>the preceding</sup> ~~any one of~~ claims ~~7 and 8~~, characterized in that they are selected from a group comprising

- i) 3-chloro-7-N,N-dimethylamino-2-methyl-5-phenyl-phenazinium chloride,  
ii) 3-bromo-7-N,N-dimethylamino-2-methyl-5-phenyl-phenazinium bromide,  
iii) 3-bromo-7-N,N-diethylamino-5-phenyl-phenazinium bromide and  
iv) 7-amino-2,8-dimethyl-3-thiocyanato-5-phenyl-phenazinium tetrafluoroborate.

9  
10. The phenazinium compounds according to any one of the preceding claims,  
obtainable according to the following method:

- 5 a) forming a diazonium compound by diazotization of a monomeric  
phenazinium compound comprising at least one primary amino group in  
the presence of mineral acid and diazotization means in a first reaction  
step,  
b) reacting the diazonium compound in a second reaction step to the  
10 halogenated or pseudohalogenated monomeric phenazinium compound  
in the presence of mineral acid and halide or pseudohalide,

wherein the first and the second reaction steps are both run in one single  
vessel.

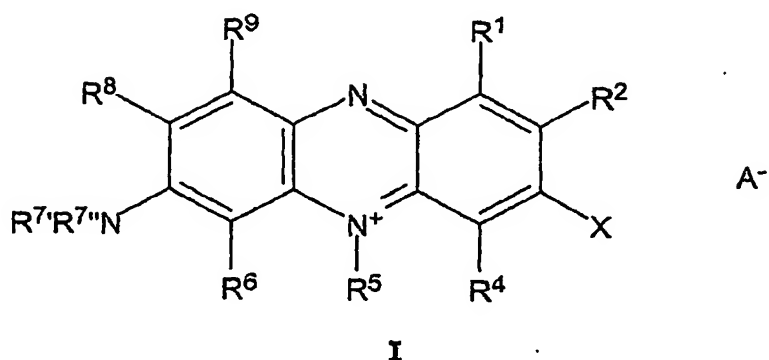
15 <sup>10</sup>  
~~11.~~ A method of preparing the halogenated or pseudohalogenated monomeric  
phenazinium compounds <sup>10</sup> ~~in accordance with one of claims 1-10,~~ comprising  
the following reaction steps:

- 20 a) forming a diazonium compound by diazotization of a monomeric  
phenazinium compound comprising at least one primary amino group in  
the presence of mineral acid and diazotization means in a first reaction  
step,  
b) reacting the diazonium compound in a second reaction step to the  
25 halogenated or pseudohalogenated monomeric phenazinium compound  
in the presence of mineral acid and halide or pseudohalide,

characterized in that the first and the second reaction steps are both run in  
one single vessel.

30 <sup>11</sup>  
<sup>12.</sup> ~~The method according to claim 11,~~ <sup>10</sup> characterized in that the mineral acid is  
selected from a group comprising hydrogen halides, sulfuric acid,  
tetrafluoroboric acid, hexafluorophosphoric acid, phosphoric acid and the  
mixtures thereof with the proviso that no hydrogen halide is used in the  
preparation of the pseudohalogenated monomeric phenazinium compounds.

of a purity of at least 85 mole-% having the following general chemical formula:



wherein

$R^1$ ,  $R^2$ ,  $R^4$ ,  $R^6$ ,  $R^{7'}$ ,  $R^{7''}$ ,  $R^8$  and  $R^9$  are selected independently of each other from a group comprising hydrogen, halogen, amino, aminoalkyl, hydroxy, cyano, thiocyanate, isothiocyanate, cyanate, isocyanate, mercapto, carboxy, the salt thereof, carbonic acid ester, sulfo, the salt thereof, sulfoester, lower alkyl, unsubstituted aryl, substituted aryl, heteroaryl and alicyclic heteroradicals,

$R^5$  is selected from a group comprising lower alkyl, unsubstituted aryl, substituted aryl and heteroaryl,

X is a halogen or a pseudo halogen and

$A^-$  is an acid anion

- 12  
13. The method according to any one of claims <sup>10</sup>11 and <sup>11</sup>12, characterized in that the diazotization means is metal nitrite or nitrosylsulfuric acid.
- 5 13  
14. The method according to claim <sup>12</sup>13, characterized in that the metal nitrite is sodium nitrite.
- 10 14  
15. The method according to any one of claims <sup>10</sup>11 - <sup>13</sup>14, characterized in that the halide is added in the form of hydrogen halide and/or in the form of a metal halide.
- 15 15  
16. The method according to claim <sup>14</sup>15, characterized in that the metal halide is selected from a group comprising transition metal halides.
- 15 16  
17. The method according to claim <sup>15</sup>16, characterized in that the transition metal halides are selected from a group comprising copper(I) halides, copper(II) halides, nickel(II) halides and iron(II) halides.
- 20 17  
18. The method according to any one of claims <sup>10</sup>11 - <sup>16</sup>17, characterized in that the halide is selected from a group comprising fluoride, chloride and bromide.
- 18  
19. The method according to any one of claims <sup>10</sup>11 - <sup>16</sup>17, characterized in that the pseudohalide is selected from a group comprising cyanate (-OCN), thiocyanate (-SCN), isocyanate (-NCO) and isothiocyanate (-NCS).
- 25 19  
20. The method according to any one of claims <sup>10</sup>11 - <sup>18</sup>19, comprising the following method steps:
- 30 i). mixing the monomeric phenazinium compounds, comprising at least one primary amino group, with the mineral acid,  
ii) next heating to a temperature above room temperature,  
iii) adding the halide or pseudohalide  
iv) adding the diazotization means.

- 20  
21. The method according to claim <sup>19</sup>20, characterized in that, in the preparation of the halogenated monomeric phenazinium compounds, the mineral acid is hydrogen halide and step iii) is eliminated.
- 5 <sup>21</sup>22. The method according to any one of claims <sup>10</sup>19-<sup>20</sup>21, characterized in that the following halogenated or pseudohalogenated monomeric phenazinium compounds are prepared:
- 10 a) 3-chloro-7-N,N-dimethylamino-2-methyl-5-phenyl-phenazinium chloride,  
b) 3-bromo-7-N,N-dimethylamino-2-methyl-5-phenyl-phenazinium bromide,  
c) 3-bromo-7-N,N-diethylamino-5-phenyl-phenazinium bromide,  
d) 7-amino-2,8-dimethyl-3-thiocyanato-5-phenyl-phenazinium tetrafluoroborate.
- 15 <sup>22</sup>23. An acidic bath for electrolytically depositing a copper deposit, containing at least one halogenated or pseudohalogenated monomeric phenazinium compound in accordance with any one of claims 1 - <sup>9</sup>10.
- 20 <sup>23</sup>24. The bath according to claim <sup>22</sup>23, characterized in that the phenazinium compounds are contained in a concentration of from 0.00005 - 0.1 g/l.
- 25 <sup>24</sup>25. The bath according to one any of claims <sup>22</sup>23 and <sup>23</sup>24, characterized in that it additionally contains compounds selected from a group comprising nitrogen-containing sulfur compounds and polymeric nitrogen compounds.
- 30 <sup>25</sup>26. The bath according to claim <sup>24</sup>25, characterized in that the concentration of the nitrogen-containing sulfur compounds and the polymeric nitrogen compounds, contained together in the bath is from 0.0001 - 0.50 g/l.
- <sup>26</sup>27. Use of the bath according to any one of claims <sup>22</sup>23 - <sup>25</sup>26 for depositing a mirror bright, leveled copper deposit for the purpose of producing decorative surfaces.

27

~~28. Use of the bath according to any one of claims 23-26 for forming a copper deposit on printed circuit board material. \* < insert text of page 33a >~~

29

~~29. Use of the bath according to any one of claims 23-26 for forming a copper~~

5

~~deposit on semiconductor substrates. \* < insert text of page 33b >~~

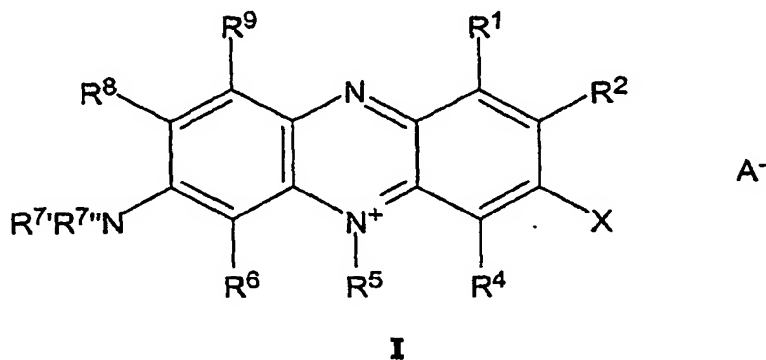
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~~30.~~ A method of electrolytically depositing a copper deposit onto a workpiece by which the workpiece and at least one anode are contacted with the bath according to one of claims <sup>22</sup>23 - <sup>25</sup>26, and a flow of electric current is generated between the workpiece and the anodes.

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page 33a

27. Use of an acid bath, containing at least one halogenated or pseudohalogenated monomeric phenazinium compound of a purity of at least 85 mole-% having the following general chemical formula:



wherein

10  $R^1, R^2, R^4, R^6, R^7, R^{7''}, R^8$  and  $R^9$  are selected independently of each other from a group comprising hydrogen, halogen, amino, aminoalkyl, hydroxy, cyano, thiocyanate, isothiocyanate, cyanate, isocyanate, mercapto, carboxy, the salt thereof, carbonic acid ester, sulfo, the salt thereof, sulfoester, lower alkyl, unsubstituted aryl, substituted aryl, heteroaryl and alicyclic heteroradicals,

15  $R^5$  is selected from a group comprising lower alkyl, unsubstituted aryl, substituted aryl and heteroaryl,

X is a halogen or a pseudo halogen and

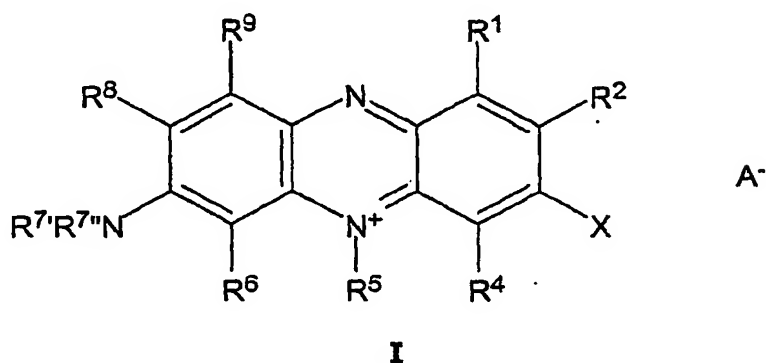
20  $A^-$  is an acid anion,

for electrolytically depositing a copper deposit on printed circuit board material.

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page 33b

28. Use of an acid bath, containing at least one halogenated or pseudohalogenated monomeric phenazinium compound of a purity of at least 85 mole-% having the following general chemical formula:



wherein

$R^1$ ,  $R^2$ ,  $R^4$ ,  $R^6$ ,  $R^7$ ,  $R^{7''}$ ,  $R^8$  and  $R^9$  are selected independently of each other from a group comprising hydrogen, halogen, amino, aminoalkyl, hydroxy, cyano, thiocyanate, isothiocyanate, cyanate, isocyanate, mercapto, carboxy, the salt thereof, carbonic acid ester, sulfo, the salt thereof, sulfoester, lower alkyl, unsubstituted aryl, substituted aryl, heteroaryl and alicyclic heteroradicals,

$R^5$  is selected from a group comprising lower alkyl, unsubstituted aryl, substituted aryl and heteroaryl,

X is a halogen or a pseudo halogen and

$A^-$  is an acid anion,

for electrolytically depositing a copper deposit on semiconductor substrates.

wherein

$R^1, R^2, R^4, R^6, R^7, R^8$  and  $R^9$  are selected independently of each other from a group comprising hydrogen, halogen, amino, aminoalkyl, hydroxy, cyano, thiocyanate, isothiocyanate, cyanate, isocyanate, mercapto, carboxy ( $\text{COO}^-$ ), the salt thereof, carbonic acid ester ( $\text{COOR}$ ), sulfo ( $\text{SO}_3^-$ ), the salt thereof, sulfoester ( $\text{SO}_3\text{R}$ ), lower alkyl, unsubstituted aryl, substituted aryl, heteroaryl and alicyclic heteroradicals,

$R^5$  is selected from a group comprising lower alkyl, unsubstituted aryl, substituted aryl and heteroaryl,

X is a halogen or a pseudohalogen and

$A^-$  is an acid anion,

\* < insert text of page 5a >

The phenazinium compounds of a purity of x mole-% as mentioned herein above, herein after and in the claims refer to a mixture of the phenazinium compounds and impurities, with the phenazinium compounds being contained in the mixture at a concentration of x mole-% and the impurities at a concentration of  $100 - x$  mole-%.

The term lower alkyl as mentioned herein above and herein after and in the claims preferably refers to  $C_1$ - to  $C_4$ -alkyl, meaning to methyl, ethyl, *n*-propyl, *iso*-propyl, *n*-butyl, *iso*-butyl and *tert*-butyl. By substituted alkyl as mentioned herein above, herein after and in the claims, sulfo- or carbonic acid-substituted alkyl is preferably meant.

Aryl as mentioned herein above or herein after and in the claims preferably refers to phenyl or polycyclic aromates such as naphthyl-1 and naphthyl-2, wherein these residues may be unsubstituted or substituted respectively. If these residues are substituted, they are more specifically substituted by alkyl, preferably by lower alkyl, halogen, hydroxy, amino, wherein amino is  $\text{NH}_2$ ,  $\text{NHR}$  or  $\text{NR}'\text{R}''$ , wherein R, R' and R'' in turn can be lower alkyl, cyano, thiocyanate and mercapto. Phenyl may more specifically be substituted at a 2-, 4- and 6-position.

*page 5a*

with the requirement that, if X is halogen, the phenazinium compounds are selected from the group, comprising

- 5
- i) 3-chloro-7-N,N-dimethylamino-2-methyl-5-phenyl-phenazinium salt,
  - ii) 3-bromo-7-N,N-dimethylamino-2-methyl-5-phenyl-phenazinium salt, and
  - iii) 3-bromo-7-N,N-diethylamino-5-phenyl-phenazinium salt.